# Air Toxics Workgroup (ATW) Discussion Paper: Clean Fuels Exemption June 11, 2013 Draft

## ORR (2011) Report Recommendation A-1(4):

R 336.1225 (R 225) should be amended and specifically include the following: Exempt clean fuels such as natural gas, low sulfur #2 fuel oil, and non-chemically treated biofuels.

## **Summary**

The ATW discussed how this exemption would help streamline the permitting process and provide an incentive for companies to use relatively cleaner-burning fuels. However, there were questions about how broad the exemption should be, and there was a need to characterize the ambient air impacts and the level of public health protection if sources were exempted from R 225 review. Therefore, toxic air contaminant (TAC) emission factors were compiled and the modeled ambient air impacts were compared to health-based screening levels. TAC emission estimates and modeled impacts are presented for engines, turbines, boilers, and process heaters that burn natural gas, low sulfur diesel, biodiesel, and wood. The ambient air concentrations of TACs for each fuel, process type and size which resulted in impacts above their respective screening levels (ITSLs and IRSLs) are provided, and for those TACs the critical toxic effects and basis for the screening levels are briefly discussed. Besides the modeling exercise for small, medium and large hypothetical facilities, TAC emissions and modeled impacts for several actual sources ("case studies") are also presented. As a result of these exercises, the ATW and AQD are much better able to make informed proposals about exempting such sources from R 225 review in permitting. Specific AQD proposals for ATW discussion are presented.

# **AQD Proposal for ATW Discussion**

It is proposed that engines, turbines, boilers and process heaters burning solely natural gas, diesel fuel (#2 fuel oil), or biodiesel, of up to 100 MMBTU/hr, may be exempted from R 225, provided that the stack height is at least 1.5 times the building height.

These exemptions are proposed because they will provide significant streamlining of the permitting process for qualifying facilities and provide an incentive for relatively cleaner fuels to be utilized, while not significantly endangering the public health. These exemptions would be significantly broader than the current AQD permitting exemptions and variance (listed below in the "Background" section). Sources that do not qualify for the proposed exemption (i.e., sources larger than 100 MMBTU/hr burning these three fuels, plus wood-burning sources of all sizes) have relatively greater modeled levels of TAC emissions and impacts exceeding screening levels, as well as relatively greater levels of anticipated community concerns, therefore it is proposed that they not be exempted from R 225.

#### **Key Terms**

**MMBTU/hour** = million British Thermal Units per hour. Emission factors are commonly presented in, or can be converted to, units of pounds of a particular TAC emitted per MMBTU (lbs/MMBTU).

**Biodiesel** is defined as a vegetable oil- or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, propyl or ethyl) esters. (The definition would be added to the Part 2 Rules.)

#### **Background**

Relevant current AQD permitting exemptions and requirements:

- a. Rule 285(g) exempts from the requirement to obtain a Permit to Install, engines that have <10 MMBTU/hour maximum heat input.
- b. Rule 282(b) exempts from the requirement to obtain a Permit to Install, several types of fuel and fuel-burning equipment, including natural gas combustion with a rated heat input capacity of not more than 50 MMBTU/hour.
- c. Emission units that do not meet any of the exemptions from the requirement to obtain a Permit to Install must currently undergo R 225 review, with one notable exception. In 2006, the AQD suspended enforcement of R 225 for certain natural gas combustion units. This one-year variance has been renewed annually since then. This variance applies to emission units that combust natural gas as fuel and that meet either of the following criteria:
  - 1. Fuel-burning equipment or natural gas fired equipment, with a maximum natural gas usage rate of 50,000 cubic feet per hour or less, where the emissions from the natural gas combustion are discharged unobstructed vertically upwards from an emissions discharge point at least 1.5 times the height of the building most influential in determining the predicted ambient impacts of the emissions.
  - 2. Air pollution control equipment, as defined by Act 451, not limited in the natural gas usage rate.

The justification for the variance for natural gas combustion engines (refer to c. above) is that some of these processes would not meet the requirements of R 225 for one or more TACs (acrolein being one), and, requiring compliance with R 225 would create an undue hardship and would be out of proportion to the benefits to be obtained by compliance. Natural gas is recognized as an environmentally beneficial, clean burning fuel; there is no better readily available alternative fuel for some sources at this time. Good engineering practice will be applied to sources that qualify for the variance to assure a continuing level of public health protection. It may be noted that the conversion factor between cubic feet of natural gas and MMBTU is: 1000 cf = 1.02 MMBTU. Therefore, the above criterion in "c.1" of 50,000 cubic feet per hour is approximately equivalent to 51 MMBTU/hr.

#### **General Approach**

A wide range of air toxics are emitted by combustion of these fuels, including VOCs, acid gases, PAHs, and aldehydes. These air toxics pose hazards including carcinogenicity and irritancy. If it can be adequately demonstrated that the ambient air impacts of air toxics from these sources are sufficiently low and that the public health will be protected, then an exemption from R 225 may be appropriate. This report summarizes the TAC emissions and modeled ambient air impacts for model facilities and the included fuels. This report also summarizes some case studies of actual permitted facilities of various sizes that utilize the evaluated fuel types, including the modeled TAC ambient air impacts and comparison of those impacts to screening levels. Additional details of both the modeling exercise and the case studies are available in a **Technical Support Document (TSD)**.

AQD staff performed modeling exercises to characterize the potential TAC impacts and public health concerns for reasonably anticipated sources and scenarios. TAC emission factors were obtained from the EPA's WebFIRE database (EPA, 2013), and air dispersion modeling was performed using EPA's AERSCREEN model. The available TAC screening levels (ITSLs and IRSLs) were used to "screen" the modeled impacts. The TACs, fuels, source types and sizes that did not pass this screen were noted, as well as the magnitude of exceedance of the screening levels (i.e., how much greater the modeled impact was, compared to the IRSL or ITSL).

One of the key concepts used to determine emissions for combustion processes is the amount of fuel burned per hour. Emission factors are commonly presented in, or can be converted to, units of pounds of a particular TAC emitted per million British Thermal Units (MMBTU), or lbs/MMBTU. In order to facilitate comparison between the processes, all emission rates were converted to lbs/MMBTU. The size of a particular fuel burning process is generally characterized in terms of heat output per hour, or MMBTU/hour.

#### <u>Methodology</u>

The modeling approach is outlined as follows:

- Appropriate air toxics emission factors were selected, for boilers, turbines, engines, and process heaters. For a particular TAC and fuel type, the highest emission factor for any of these four source types was selected for the subsequent modeling and evaluation.
- 2. Only indirect combustion sources (processes where the products of combustion do not come in direct contact with a raw material being processed) were included.
- 3. The fuel types evaluated included natural gas, diesel fuel (a.k.a., No. 2 fuel oil<sup>1</sup>), wood/bark, and biodiesel. EPA does not have emission factors (EFs) for biodiesel in WebFIRE, therefore a literature search was performed.
- 4. For the purposes of this exercise, modeling was performed for relatively small, medium, and large source sizes (with representative values of 50 MMBTU/hour, 100 MMBTU/hour, and 500 MMBTU/hour, respectively).
- 5. The stack heights for the modeled small, medium, and large sources were 40', 60', and 80', respectively. These are believed to be fairly representative, for the purposes of this exercise. Other facility parameters (e.g., exit velocity (10 m/s); temperature (250F)) are believed to be reasonable values.
- 6. The assumed ratio of the stack height and building height (Hs/Hb) was 1.5.
- 7. The modeling grid used 25 m spacing, with 50 m from the stack to the nearest receptor.
- 8. The building dimensions were 100' X 100', and the stack was placed at the center of the building. Therefore, the nearest modeling receptor was approximately 150' from the stack and 100' from the edge of the building.

It should be noted that this methodology utilized some conservative elements and assumptions, including:

1. The highest available and appropriate emission factor was selected for each TAC, across the four source types, for each fuel type evaluated. In some cases, the highest

<sup>&</sup>lt;sup>1</sup> The predominant form of No. 2 fuel oil in use by Michigan facilities today is ultra-low sulfur diesel fuel. However, this is not an important distinction because the available air toxics emission factors do not differentiate based on the sulfur grade of the fuel.

EF had a quality rating that was lower than other EFs, e.g.: diesel, benzene ("E" highest EF was 17X higher than the "C" lowest EF; diesel, beryllium ("E" highest EF was 10X higher than the "D" lowest EF. In two cases, the highest EF utilized was actually reported as a "<" value: diesel, acrolein; and, diesel, arsenic. Details are provided in the TSD.

- 2. The emission factors utilized were for uncontrolled emission sources. Although some actual sources may have emission limits or controls, not all will, and the proposed exemption does not require emission control equipment. It may be noted, for example, that natural gas boilers may be subject to several regulations, including the following:
  - R 301 & 331 Opacity and particulate matter emissions.
  - Part 4 Sulfur Compounds.
  - o R 702 BACT for VOCs
  - Part 9 Preventative maintenance and SU/SD emissions
  - NAAQS and PSD Increment compliance
  - Demonstration of compliance with applicable federal new source performance standards (NSPS), including subparts da, db, and/or dc.
  - Demonstration of compliance with applicable federal national emissions standards for hazardous air pollutants (NESHAPS), including subparts ddddd or jijiji.
  - PSD top-down BACT for all affected pollutants.
- 3. The nearest receptor point was fairly close to the building (100 ft), and the receptor point with the maximum modeled impact was selected for comparison to screening levels.
- 4. The model used to estimate ambient air impacts was AERSCREEN. This is a screening model, designed to give conservative results that would be equal to or greater than the results that would be expected from a refined model (Haywood, personal communication).
- 5. The public exposure potential was assumed to be continuous, at the point of maximum modeled impact. This may be fairly realistic for screening levels with short averaging times (e.g., 1-24 hr), but this is generally conservative for annual averaging times. For cancer risk assessment and other critical effects associated with chronic exposure, assumed continuous lifetime exposure at the point of maximum modeled impact is conservative.
- 6. Air toxics screening levels generally have uncertainty, and are designed to be protective of the public including sensitive subgroups. Therefore, a modeled ITSL exceedance that is small in magnitude would not necessarily be expected to result in adverse health effects in a community. Cancer risk estimates are based on generally conservative extrapolation to low-risk estimates, using "plausible upper-bound" modeling, and, IRSLs are associated with a plausible upper bound lifetime incremental risk (1 in one million) that is considered acceptably low in the AQD's Permit to Install regulatory program.

It should also be noted that this methodology utilized some nonconservative elements and assumptions, including:

- Background (aggregate) exposures to the same TACs are not accounted for. (Typical R 225 review would also not account for this; R 228 and R 226(d) reviews may account for it.)
- 2. Cumulative interactive exposures (multiple TACs) from co-emitted TACs and background exposures are not accounted for. (Typical R 225 review would also not account for this; R 228 and R 226(d) reviews may account for it.)

- 3. Potentially higher intermittent emissions during start-up, shutdown and malfunction episodes are not accounted for.
- 4. A single source scenario is evaluated in the methodology, however, a facility could potentially have multiple such engines, turbines, boilers and process heaters. (Typical R 225 review would also not account for this, unless the multiple units are part of the same project in the PTI application, or, if compliance with a SRSL is being demonstrated. R 228 and R 226(d) reviews may account for it.)

#### **Results**

The modeling exercise was a screening approach that was intended to identify fuel types and source sizes that may *potentially* result in modeled ambient air impacts that exceed ITSLs or IRSLs, based on the screening methodology. The screening exercise provides estimated SL exceedances that *could* occur, not exceedances that would be *expected* to occur. In those cases where a SL is exceeded, the following Tables also present the magnitude by which the modeled impact exceeds the ITSL or IRSL ("magnitude of SL exceedance"). Modeled ambient air impacts that exceed their screening levels should not necessarily be interpreted to mean that unacceptable public health risks exist and that an exemption is inappropriate. It does indicate the sources, fuels and TACs that warrant more focused consideration.

#### A. Natural gas

A total of 76 TACs had available appropriate emission factors for natural gas, for at least one of the four source types. Most EFs were for engines or boilers; process heaters had EFs only for formaldehyde. Cumulative (additive) cancer risks for small, medium and large sources were 9, 12, and 43 in one million, respectively. The TACs that had maximum modeled impacts exceeding an ITSL or IRSL were as follows:

Source Size (MMBTU/hr)	Chemical Name	SL* Type	SL (µg/m³)	AT**	Magnitude of SL exceedance***	Process Type
50	1,3-Butadiene	IRSL	0.03	annual	3.0	Recip engine
50	Acetaldehyde	IRSL	0.5	annual	1.8	Recip engine
50	Acrolein	ITSL	5	1 hr	1.7	Recip engine
50	Acrolein	ITSL	0.02	annual	42.2	Recip engine
50	Ethylene dibromide	IRSL	0.002	annual	4.0	Recip engine
100	1,3-butadiene	IRSL	0.03	Annual	3.9	Recip engine
100	Acetaldehyde	IRSL	0.5	Annual	2.4	Recip engine
100	Acrolein	ITSL	5	1 hr	2.2	Recip engine
100	Acrolein	ITSL	0.02	Annual	56	Recip engine
100	Ethylene dibromide	IRSL	0.002	Annual	5.3	Recip engine
500	1,1,2,2- Tetrachloroethane	IRSL	0.02	annual	1.7	Recip engine
500	1,3-Butadiene	IRSL	0.03	annual	13.9	Recip engine
500	1,3-Butadiene	ITSL	2	24 hr	1.25	Recip engine
500	Acetaldehyde	ITSL	9	24 hr	2.8	Recip engine
500	Acetaldehyde	IRSL	0.5	annual	8.5	Recip engine
500	Acrolein	ITSL	5	1 hr	7.9	Recip engine
500	Acrolein	ITSL	0.02	annual	198.0	Recip engine
500	Ethylene dibromide	IRSL	0.002	annual	18.6	Recip engine

<sup>\*</sup>Screening Level: Initial Threshold Screening Level (ITSL); Initial Risk Screening Level (IRSL)

<sup>\*\*</sup> AT = Averaging Time associated with the Screening Level

<sup>\*\*\*</sup>The magnitude of the IRSL exceedance can also be characterized as the incremental lifetime cancer risk in 1 million, and the magnitude of the ITSL exceedance can also be called the noncancer Hazard Quotient (HQ).

# B. Diesel fuel (#2 fuel oil)

A total of 36 TACs had available appropriate emission factors for diesel fuel, for at least one of the four source types. Cumulative (additive) cancer risks for small, medium and large sources were 8, 13, and 56 in one million, respectively. The TACs that had maximum modeled impacts exceeding an ITSL or IRSL were as follows:

Source Size (MMBTU/hr)	Chemical Name	SL* Type	SL (µg/m³)	AT**	Magnitude of SL exceedance***	Process Type
50	Arsenic	IRSL	0.0002	Annual	6.0	Engine turbine
50	Benzene	IRSL	0.1	Annual	1.01	Engine recip.
50	Chromium VI	IRSL	8.3E-5	Annual	1.44	Engine turbine
50	Manganese	ITSL	0.05	Annual	1.71	Engine turbine
100	Arsenic	IRSL	0.0002	Annual	7.9	Engine turbine
100	Benzene	IRSL	0.1	Annual	1.3	Engine recip.
100	Beryllium	IRSL	0.0004	Annual	1.1	Boiler
100	Cadmium	IRSL	0.0006	Annual	1.2	Engine turbine
100	Chromium VI	IRSL	8.3E-4	Annual	1.9	Engine turbine
100	Manganese	ITSL	0.05	Annual	2.3	Engine turbine
500	Acetaldehyde	IRSL	0.5	Annual	1.1	Engine Recip
500	Acrolein	ITSL	0.02	Annual	2.4	Engine Recip
500	Arsenic	IRSL	0.0002	Annual	28.0	Engine turbine
500	Benzene	IRSL	0.1	Annual	4.7	Engine Recip
500	Beryllium	IRSL	0.0004	Annual	3.8	Boiler
500	Cadmium	IRSL	0.0006	Annual	4.1	Engine turbine
500	Chromium VI	IRSL	8.3E-5	Annual	6.7	Engine turbine
500	Formaldehyde	IRSL	0.08	Annual	7.5	Engine Recip
500	Manganese	ITSL	0.05	Annual	8.0	Engine turbine

<sup>\*</sup>Screening Level: Initial Threshold Screening Level (ITSL); Initial Risk Screening Level (IRSL)

<sup>\*\*</sup> AT = Averaging Time associated with Screening Level

<sup>\*\*\*</sup> The magnitude of the IRSL exceedance can also be characterized as the incremental lifetime cancer risk in 1 million, and the magnitude of the ITSL exceedance can also be called the noncancer Hazard Quotient (HQ).

#### C. Wood

A total of 129 TAC Emission Factors were available for wood fired boilers. Cumulative (additive) cancer risks for small, medium and large sources were 27, 37, and 141 in one million, respectively. The TACs that had maximum modeled impacts exceeding an ITSL or IRSL were as follows:

Source Size (MMBTU/hr)	Chemical Name	SL* Type	SL (µg/m³)	AT**	Magnitude of SL exceedance***	Process Type
50	Acrolein	ITSL	0.02	annual	21.72	Wood boiler
50	Arsenic	IRSL	0.0002	Annual	11.95	Wood boiler
50	Benzene	IRSL	0.1	Annual	4.56	Wood boiler
50	Chromium VI	IRSL	8.5E-5	Annual	4.58	Wood boiler
50	Formaldehyde	IRSL	0.08	Annual	5.97	Wood boiler
50	Manganese	ITSL	0.05	annual	3.48	Wood boiler
50	Silver	ITSL	0.1	8 hr	16.62	Wood boiler
100	Acrolein	ITSL	0.02	annual	28.78	Wood boiler
100	Acrolein	ITSL	5	1 hr	1.15	Wood boiler
100	Arsenic	IRSL	0.0002	Annual	15.83	Wood boiler
100	Benzene	IRSL	0.1	Annual	6.04	Wood boiler
100	Chromium VI	IRSL	8.5E-5	Annual	6.07	Wood boiler
100	Formaldehyde	IRSL	0.08	Annual	7.91	Wood boiler
100	Manganese	ITSL	0.05	annual	4.60	Wood boiler
100	Nickel	IRSL	0.0042	Annual	1.13	Wood boiler
100	Silver	ITSL	0.1	8 hr	22.02	Wood boiler
500	Acrolein	ITSL	0.02	annual	101.80	Wood boiler
500	Acrolein	ITSL	5	1 hr	4.07	Wood boiler
500	Arsenic	IRSL	0.0002	Annual	55.99	Wood boiler
500	Benzene	IRSL	0.1	Annual	21.38	Wood boiler
500	Benzo (a) pyrene	IRSL	0.0005	Annual	2.65	Wood boiler
500	Beryllium	IRSL	0.0004	Annual	1.40	Wood boiler
500	Cadmium	IRSL	0.0006	Annual	3.48	Wood boiler
500	Chlorine	ITSL	0.3	annual	1.34	Wood boiler
500	Chromium VI	IRSL	8.3E-5	Annual	21.46	Wood boiler
500	Chromium VI	ITSL	0.008	24 hr	1.34	Wood boiler
500	Formaldehyde	IRSL	0.08	Annual	28.00	Wood boiler
500	Formaldehyde	ITSL	9	8 hr	2.24	Wood boiler
500	Manganese	ITSL	0.05	annual	16.29	Wood boiler
500	Nickel	IRSL	0.0042	Annual	4.00	Wood boiler
500	Silver	ITSL	0.1	8 hr	77.86	Wood boiler
500	Total Dioxin TEQ****	IRSL	2.3E-08	Annual	2.66	Wood boiler

<sup>\*</sup>Screening Level: Initial Threshold Screening Level (ITSL); Initial Risk Screening Level (IRSL)

<sup>\*\*</sup> AT = Averaging Time associated with Screening Level

<sup>\*\*\*</sup> The magnitude of the IRSL exceedance can also be characterized as the incremental lifetime cancer risk in 1 million, and the magnitude of the ITSL exceedance can also be called the noncancer Hazard Quotient (HQ).

<sup>\*\*\*\*</sup> The EF for total dioxin TEQ is based on a boiler with a multicyclone air pollution control device. It was assumed that very little dioxin-like compounds would be captured using this device, therefore, it was deemed appropriate to use this EF as an "uncontrolled" process for the purposes of this assessment. EPA (WebFire) has EF for uncontrolled wood boilers for dioxins

congeners which group dioxins by chlorine number. AQD was unable to allocate carcinogenic potency of these groupings because not all the individual congeners within a group are carcinogenic and/or do not have toxic equivalency factors.

#### D. Biodiesel

EPA does not have EFs for biodiesel in WebFIRE. A study by EPA (2008) was performed and the resulting EFs were used for this exercise. A total of 157 TAC Emission Factors were available for biodiesel fired boilers burning either soy or animal biodiesel. EFs for metals and acrolein were not available for biodiesel boilers. Another study (Cosseron et al., 2011) suggests that carbonyl compounds may be emitted at a higher rate than for petroleum diesel. Cumulative (additive) cancer risks for small, medium and large sources were 4, 6, and 23 in one million, respectively. The TACs that had maximum modeled impacts exceeding an ITSL or IRSL were as follows:

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Source Size (MMBTU/hr)	Chemical Name	SL* Type	SL (µg/m³)	AT**	Magnitude of SL exceedance***	Biodiesel Boiler Fuel Type	
50	Formaldehyde	IRSL	0.08	Annual	4.19	SOY	
100	Formaldehyde	IRSL	0.08	Annual	5.55	SOY	
500	Formaldehyde	ITSL	9	8 hr	1.57	SOY	
500	Formaldehyde	IRSL	0.08	Annual	19.62	SOY	
500	Acetaldehyde	ITSL	9	24 hr	1.15	SOY	
500	Acetaldehyde	IRSL	0.5	Annual	3.45	SOY	
500	Formaldehyde	IRSL	0.08	Annual	1.88	Animal	

<sup>\*</sup>Screening Level: Initial Threshold Screening Level (ITSL); Initial Risk Screening Level (IRSL)

Further details of the screening levels that were exceeded by the maximum modeled impacts for any of the fuel types are provided in **Appendix 1**.

The case studies of actual permitted sources are described in the **Technical Support Document**. In all cases, the modeled impacts met the SLs, but it is interesting to note the TACs that had ambient air impacts with the highest percentages of the SLs. Five sources burning natural gas were reviewed and summarized: one large source had relatively higher impacts (as % of SLs) for formaldehyde (72%), PAHs (36%), cadmium (15%), hexavalent chrome (12%), arsenic (8%), nickel (4%) and acrolein (2.6%), etc. Four diesel sources were summarized: the relatively higher impacts (as % of SLs) were for benzene (up to 37%), formaldehyde (up to 6.9%), benzo(a)pyrene equivalents (26%), naphthalene (up to 23%), and acrolein (up to 18%), etc. Four wood-burning sources were summarized: the relatively higher impacts (as % of SLs) were for silver (97.7%), chrysene (75%), acrolein (56%), formaldehyde (47%), hexavalent chrome (41%), manganese (27%), chlorine (27%), naphthalene (18%), 1,3-butadiene (17%), arsenic(28%), ethylene dibromide (10%), and acetaldehyde (10%), etc.

#### **Discussion**

The rationale for potentially exempting from R 225 certain sources that burn certain fuels was evaluated by modeling hypothetical facilities, and by reviewing some actual case study facilities. Although there are uncertainties in the health-based screening levels and in the methodology utilized in the modeling exercise, the results may support reasonable risk management decisions for exempting certain sources from future R 225 reviews in Permit to

<sup>\*\*</sup> AT = Averaging Time associated with Screening Level

<sup>\*\*\*</sup> The magnitude of the IRSL exceedance can also be characterized as the incremental lifetime cancer risk in 1 million, and the magnitude of the ITSL exceedance can also be called the noncancer Hazard Quotient (HQ).

Install applications. Significant streamlining of permit applications and permit reviews, and an incentive for sources to utilize relatively cleaner fuels, would be the benefit of a R 225 exemption. Based on the findings, it appears reasonable to propose R 225 exemptions for natural gas, diesel fuel (#2 fuel oil) and biodiesel combustion sources of up to 100 MMBTU/hr that have a stack height-to-building height ratio of at least 1.5. These exemptions are proposed to apply to single-fuel or multi-fuel units burning only these fuels. And, diesel fuel is intended to mean only non-recycled diesel fule (not recycled used oil).

These proposed exemptions would be significantly broader than the current AQD permitting exemptions and variance (listed in the "Background" section). Sources that do not qualify for the proposed exemptions (i.e., sources larger than 100 MMBTU burning these three fuels, plus wood-burning sources of all sizes) have relatively greater modeled levels of TAC emissions and impacts exceeding screening levels as well as relatively greater levels of anticipated community concerns, therefore it is proposed that they not be exempted from R 225.

It may also be noted that if an applicant is applying for a PTI for a unit that is not exempt from R 225, and is attempting to demonstrate compliance with a SRSL for a TAC, then they must account for facilitywide emissions of that TAC, including emissions from units that are exempt from R 225 or exempt from requiring a PTI. That approach is consistent with AQD's past policy.

# Appendix 1. Summary of the Screening Levels That Were Exceeded By Modeled Impacts

#### Noncarcinogenic Effects

Eight TACs had ITSLs that were exceeded when impacts were modeled, for certain size, fuel and process types. Modeled impacts are listed below as Predicted Ambient Impacts (PAIs).

## 1) Acrolein

- a. Acrolein Acute SL: 5 μg/m³ with a 1-hr averaging time
  - The Acute SL for acrolein was exceeded for these fuels and size processes:

Fuel	Size	PAI* (µg/m³)	Ratio of PAI/ITSL	Ratio of PAI/14 µg/m³
Wood	Medium	5.76	1.2	0.41
Wood	Large	20.36	4.1	0.60
Nat Gas	Small	8.45	1.7	0.80
Nat Gas	Medium	11.20	2.2	1.45
Nat Gas	Large	39.60	7.9	2.83

ii. The basis of the acute acrolein ITSL is a study (Darley et al., 1960) where 36 healthy human (student) volunteers were exposed (eyes only) to 140 µg/m<sup>3</sup> for 5 minutes. Severity of eye irritation was measured subjectively in test subjects and controls as 0=no irritation, 1=mild and 2=severe. The low dose of 140 µg/m<sup>3</sup> had an average irritation score of 0.47 compared to control subjects of 0.36. More significant irritancy at the higher dose of 3380 µg/m<sup>3</sup> had an average eye irritation score of 1.2, which is slightly higher than mild irritation. The ITSL derivation utilized a total uncertainty factor of 30, including 10 for human variability and 3 to account for mild irritation effects at the low dose. Another benchmark could be calculated as 14 µg/m<sup>3</sup> (using a total uncertainty factor of 10 for protection of sensitive individuals and duration uncertainty). In another key study (Weber-Tschopp et al., 1977), eye irritation occurred in people exposed to 210 ug/m<sup>3</sup> and irritation of the nose and throat occurred at 690 ug/m<sup>3</sup>, within a short time (5 minutes up to 1 hour). Applying an uncertainty factor of 30 (10 for human variability and 3 for irritant effects) to these effect levels would result in additional benchmarks of 7 and 23 ug/m<sup>3</sup>. There is also a concern that sensitive subgroups, such as asthmatics, may be affected by irritants such as acrolein, as well as the additive effects from other TACs that may be co-emitted. The modeled acrolein impacts of the large natural gas source (39.6 ug/m<sup>3</sup>, 1 hr AT) pose a relatively greater level of concern. Peak impacts for even shorter time periods (e.g., 5 minutes) would be expected to be even higher, and as shown in the key studies, could elicit effects over such short periods.

- b. Acrolein Chronic SL: 0.02 μg/m³ with an annual averaging time.
  - i. Fuel, Size and Process Scenarios

Fuel	Size	Worst Process	PAI (µg/m3)	Ratio PAI to ITSL
Diesel	Large	Reciprocating Engine	0.05	2.4
Wood	Small	boiler	0.43	21.7
Wood	Medium	boiler	0.58	28.8
Nat Gas	Small	Reciprocating Engine	0.84	42.2
Nat Gas	Medium	Reciprocating Engine	1.12	56.0
Wood	Large	boiler	2.04	101.8
Nat Gas	Large	Reciprocating Engine	3.96	198.0

- ii. The chronic ITSL for acrolein is based on an EPA RfC, which is based on a subchronic (3 month) rat inhalation study. Histopathologic changes described as "slightly affected" were found in the nasal cavity of 1 of 12 rats exposed to the lowest dose of 0.4 ppm (900 ug/m3). The duration adjusted LOAEL (6 hours per day; 5 days per week; 6/24x5/7) = 160 µg/m<sup>3</sup>. A total uncertainty factor of 1000 was applied. The animal dose was also adjusted to a human equivalent concentration using a regional gas dose ratio (RGDR) of 0.14. However, recent EPA guidance states that acrolein is among one of a number of compounds that act on the nasal passages via a mechanism in which the RGDR should be equal to 1 (i.e., the dose in rats equals the dose in humans). An alternative ITSL calculation reflecting this change in the EPA recommended approach would therefore be 0.16 µg/m³ with an annual averaging time. The AQD will proceed to make that change to the ITSL. It is also noted that California and Texas have chronic benchmarks, based on a more recent (2008) study, at 0.35 and 0.5 ug/m<sup>3</sup>, respectively, based on a rat noeffect-level of 458 ug/m<sup>3</sup>. The highest impact scenario comes from the large natural gas reciprocating engine scenario, with a fenceline ambient air concentration of ~4 μg/m³ (annual averaging time). This summary of the underlying key study and the application of uncertainty factors suggests that the maximum modeled impacts exceed the health protective benchmarks by a large margin, however there is a large uncertainty factor utilized in deriving the benchmark. The results indicate some concern for chronic nasal irritant effects, particularly for larger wood and natural gas sources.
- 2) Butadiene: Chronic ITSL =  $2 \mu g/m^3$  with 24-hr averaging time.
  - a. The ITSL was modestly exceeded for one scenario: Large Natural Gas Reciprocating engine at 2.5 μg/m³.
  - b. According to Rule 232(21)(a), the 24-hr averaging time is applied to the EPA RfC of 2 μg/m³ which is the basis of the ITSL. Because EPA used a long-term study as the basis of the RfC and applied methodology consistent with calculating a long-term health benchmark (i.e., chronic) it may be more appropriate to use an annual averaging time with the ITSL. If impacts are compared to 2 μg/m³ with an annual averaging time, then the annual impacts for Butadiene are 0.4 μg/m³ and are below the benchmark.

- 3) Acetaldehyde: Chronic ITSL =  $9 \mu g/m^3$  with 24 hour averaging time.
  - a. The ITSL was exceeded for one scenario: Large Natural Gas Reciprocating engine at 25.5 μg/m³. (2.83x above the ITSL)
  - b. According to Rule 232(21)(a), the 24-hr averaging time is applied to the EPA RfC of 9  $\mu$ g/m³ which is the basis of the ITSL. Because EPA used a long-term study as the basis of the RfC and applied methodology consistent with calculating a long-term health benchmark (i.e., chronic) it may be more appropriate to use an annual averaging time with the ITSL. If impacts are compared to 9  $\mu$ g/m³ with an annual averaging time, the annual impacts for acetaldehyde are 4.3  $\mu$ g/m³ and are below the benchmark.
- 4) Chlorine: Chronic ITSL =  $0.3 \mu g/m^3$  with annual averaging time
  - a. The impact of 0.4 μg/m³ modestly exceeded the ITSL for one scenario: Large wood fired boiler. This is 1.3x ITSL.
  - b. The study used to derive the ITSL exposed rats to various concentrations of chlorine; the lowest dose of 0.4 ppm (1.1 mg/m³) produced significant nasal lesions. The benchmark dose methodology was used to extrapolate to a NOAEL of 0.2 mg/m³ (200 μg/m³), then duration adjusted (6/24x 5/7) to get 0.042 mg/m³ (42 μg/m³). A further adjustment was made to account for the differences between rat and human nasal dosimetry, with a factor of 0.2 for the regional gas dose ratio (RGDR) to obtain a point of departure of 8.4 μg/m³. A total UF of 30 was used: 3 for animal to human and 10 for sensitive individuals to get ITSL of 0.3 (rounded from 0.28 μg/m³). Recent analysis comparing the nasal region of rat to humans indicates, "a larger portion of inspired air passed through olfactory-lined regions in the rat than in the monkey or human." (Kimbell, 2006). Given that the rat nasal region gets a higher dose than humans then the RGDR could default to 1. If the RGDR of 1 is used, the RfC and ITSL would 1.4 μg/m³. The chlorine impact from large wood fired boilers is 0.4 μg/m³ and is less than the adjusted chlorine benchmark of 1.4 μg/m³
- 5) Chromium IV (hexavalent chromium): Chronic ITSL = 0.01 ug/m3 with a 24-hr averaging time.
  - a. Large wood fired boiler produced an impact of 0.0107 μg/m³ with a 24-hr average; this is slightly above the ITSL.
  - b. As mentioned before, the averaging time for chronic benchmarks may be more appropriately set at annual averaging. The annual impact of Chromium IV is 0.00178 μg/m³, which is less than the adjusted benchmark of 0.01 ug/m³ with annual averaging.
- 6) Formaldehyde: Acute ITSL = 9 ug/m³ with 8-hr averaging time
  - a. Large wood fired boiler produced an impact of 20  $\mu$ g/m³ with an 8-hr average, which is 2.3x higher than the ITSL.
  - b. The ITSL was derived from a human occupational study where workers were exposed for 8 hrs/day for an average of 10 years. The observed effects were: Nasal obstruction and discomfort, lower airway discomfort, and eye irritation at the LOAEL of 0.26 mg/m³. A NOAEL of 0.09 mg/m³ was also identified. The formaldehyde impact is roughly 3x lower than the NOAEL and 13x lower than the LOAEL.

- 7) Manganese: Chronic ITSL =  $0.05 \mu g/m^3$  annual averaging time (based on the EPA RfC).
  - a. Fuel, process and size scenarios where impacts exceeded ITSL:

Fuel	Size	Worst Process	PAI Impacts (µg/m3)	Ratio to SL
diesel	Small	Engine Turbine	0.09	1.72
diesel	Medium	Engine Turbine	0.11	2.27
diesel	Large	Engine Turbine	0.40	8.04
wood	Small	boiler	0.17	3.48
wood	Medium	boiler	0.23	4.60
wood	Large	boiler	0.81	16.29

- b. The ITSL is based on an occupational study where neurological effects were observed at an effect level of 150  $\mu$ g/m³, which was duration adjusted to 50  $\mu$ g/m³, and an uncertainty factor of 1000 was applied. It may be noted that EPA's RfC is under reevaluation by EPA, and, the ATSDR recently increased their chronic inhalation Minimal Risk Level (MRL) to 0.3  $\mu$ g/m³. The ITSL exceedances raise some concern, particularly for large diesel and all sizes of wood-fired sources.
- 8) Silver: Acute ITSL =  $0.1 \mu g/m^3 8 hr$ 
  - a. Wood boilers of all sizes (small, medium and large) had impacts of 1.7, 2.2 and 7.8 μg/m³, respectively (magnitude of ITSL exceedance = 17, 22 and 78, respectively).
  - b. The ITSL is based on an occupational exposure limit (OEL) of 10 μg/m³ for soluble silver compounds, in order to prevent argyria. Silver dust has an OEL of 100 μg/m³. The ITSL is derived by dividing the soluble silver OEL by 100. Argyria is caused by chronic intake of silver, resulting in an accumulation of silver or silver sulfide particles in the skin and eyes. Argyria is generally believed to be irreversible. The effect is objectionable, but generally not regarded as physically harmful. The American Conference of Governmental and Industrial Hygienists (ACGIH) stated that the photographic industry's use of silver nitrate indicated that no cases of argyria or other adverse effects have appeared where average exposures were about 40 to 60 μg/m³ with values as high as about 150 μg/m³. The highest impact of 7.8 μg/m³ is below the OEL of 10 μg/m³ and is below a reported no effect level of approximately 40 μg/m³.

#### **Carcinogenic Effects**

Twelve TACs were modeled to have impacts associated with incremental lifetime cancer risk

estimates of at least 1 in one million, for a specific fuel, process type and size:

			IRSL		Risk		Comparison
Fuel	Size	Chemical	(µg/m³)	<b>Worst Process</b>	PAI* (µg/m3)	per Million	Comparison to SRSL
N . O		1,1,2,2-	0.00	Б Е.	0.004		0001
Nat Gas	Large	Tetrachloroethane	0.02	Reciprocating Engine	0.034	2	<srsl< td=""></srsl<>
Nat Gas	Small	1,3-Butadiene	0.03	Reciprocating Engine	0.089	3	<srsl< td=""></srsl<>
Nat Gas	Medium	1,3-Butadiene	0.03	Reciprocating Engine	0.12	4	<srsl< td=""></srsl<>
Nat Gas	Large	1,3-Butadiene	0.03	Reciprocating Engine	0.42	14	> SRSL
Diesel	Large	Acetaldehyde	0.5	Reciprocating Engine	0.54	1.1	<srsl< td=""></srsl<>
Nat Gas	Small	Acetaldehyde	0.5	Reciprocating Engine	0.91	2	<srsl< td=""></srsl<>
Nat Gas	Medium	Acetaldehyde	0.5	Reciprocating Engine	1.2	2	<srsl< td=""></srsl<>
Soy BD	Large	Acetaldehyde	0.5	Boiler	1.7	3	<srsl< td=""></srsl<>
Nat Gas	Large	Acetaldehyde	0.5	Reciprocating Engine	4.3	9	<srsl< td=""></srsl<>
Diesel	Small	Arsenic	2E-4	Engine Turbine	0.0012	6	<srsl< td=""></srsl<>
Diesel	Medium	Arsenic	2E-4	Engine Turbine	0.0016	8	<srsl< td=""></srsl<>
Wood	Small	Arsenic	2E-4	Boiler	0.0024	12	> SRSL
Wood	Medium	Arsenic	2E-4	Boiler	0.0032	16	> SRSL
Diesel	Large	Arsenic	2E-4	Engine Turbine	0.0056	28	> SRSL
Wood	Large	Arsenic	2E-4	Boiler	0.011	56	> SRSL
Diesel	Small	Benzene	0.1	Reciprocating Engine	0.10	1.01	<srsl< td=""></srsl<>
Diesel	Medium	Benzene	0.1	Reciprocating Engine	0.13	1.3	<srsl< td=""></srsl<>
Wood	Small	Benzene	0.1	Boiler	0.46	5	<srsl< td=""></srsl<>
Diesel	Large	Benzene	0.1	Reciprocating Engine	0.47	5	<srsl< td=""></srsl<>
Wood	Medium	Benzene	0.1	Boiler	0.60	6	<srsl< td=""></srsl<>
Wood	Large	Benzene	0.1	Boiler	2.1	21	> SRSL
Wood	Large	Benzo (a) pyrene	5E-4	Boiler	0.0013	3	<srsl< td=""></srsl<>
Diesel	Medium	Beryllium	4E-4	Boiler	0.00043	1.1	<srsl< td=""></srsl<>
Wood	Large	Beryllium	4E-4	Boiler	0.00056	1.4	<srsl< td=""></srsl<>
Diesel	Large	Beryllium	4E-4	Boiler	0.0015	4	<srsl< td=""></srsl<>
Diesel	Medium	Cadmium	6E-4	Engine Turbine	0.00069	1.2	<srsl< td=""></srsl<>
Wood	Large	Cadmium	6E-4	Boiler	0.0021	3	<srsl< td=""></srsl<>
Diesel	Large	Cadmium	6E-4	Engine Turbine	0.0024	4	<srsl< td=""></srsl<>
Diesel	Small	Chromium (VI)	8.3E-5	Engine Turbine	0.00012	1.4	<srsl< td=""></srsl<>
Diesel	Medium	Chromium (VI)	8.3E-5	Engine Turbine	0.00012	2	<srsl< td=""></srsl<>
Wood	Small	Chromium (VI)	8.3E-5	Boiler	0.00038	5	<srsl< td=""></srsl<>
	Medium	Chromium (VI)		Boiler	<del> </del>	6	<srsl< td=""></srsl<>
Wood			8.3E-5		0.00050		
Diesel	Large	Chromium (VI)	8.3E-5	Engine Turbine	0.00056	7 21	<srsl &gt; SRSL</srsl 
Wood	Large	Chromium (VI)	8.3E-5	Boiler	0.0018		
Nat Gas	Small	Ethylene Dibromide Ethylene Dibromide	0.002	Reciprocating Engine	0.0080	4	<srsl< td=""></srsl<>
Nat Gas	Medium		0.002	Reciprocating Engine	0.011	5	<srsl< td=""></srsl<>
Nat Gas	Large	Ethylene Dibromide	0.002	Reciprocating Engine	0.037	19	> SRSL
Animal BD	Largo	Formaldehyde	0.00	Boiler	0.15	2	<srsl< td=""></srsl<>
	Large	Formaldehyde	0.08		0.15	2	
Diesel	Large Small	Formaldehyde	0.08	Reciprocating Engine	0.6	7.5	<srsl< td=""></srsl<>
Soy BD		· · · · · · · · · · · · · · · · · · ·	0.08	Boiler	0.33	4	<srsl< td=""></srsl<>
Soy BD	Medium	Formaldehyde	0.08	Boiler	0.44	6	<srsl< td=""></srsl<>
Wood	Small	Formaldehyde	0.08	Boiler	0.48	6	<srsl< td=""></srsl<>
Wood	Medium	Formaldehyde	0.08	Boiler	0.63	8	<srsl< td=""></srsl<>
Soy BD	Large	Formaldehyde	0.08	Boiler	1.6	20	> SRSL
Wood	Large	Formaldehyde	0.08	Boiler	2.2	28	> SRSL
Wood	Medium	Nickel	0.0042	Boiler	0.0047	1.1	<srsl< td=""></srsl<>
Wood	Large	Nickel	0.0042	Boiler	0.017	4	<srsl< td=""></srsl<>

It may be noted that several of the TAC modeled impacts also exceeded the SRSL. None exceeded a 1 in 10,000 risk level. Cumulative (additive) cancer risk is noted previously, in the Results section for each fuel type.

#### REFERENCES

Cosseron AF, Bennadji H, Leyseens G, Coniglio L, Daou T, Tschamber V. (2011) Efficiency of a 4 way catalytic converter towards carbonyl compounds and fine particles emission generated by combustion of biodiesels in a generator. Proceedings of the 12<sup>th</sup> International Conference on Environmental Science and Technology, Rhodes, Greece, 8-10 September 2011. A351-A358. Downloaded 4-April-2013:

EPA, 2008. Characterizing Emissions from the Combustion of Biofuels Prepared by C. Andrew Miller. September 2008 U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, NC. EPA/600/R-08/069. Excel data files

http://cfpub.epa.gov/si/si\_public\_file\_download.cfm?p\_download\_id=500086

http://www.srcosmos.gr/srcosmos/showpub.aspx?aa=15011

obtained via personal communication are available.

EPA, 2013. WebFIRE. On-line Database. Technology Transfer Network Clearinghouse for Inventories & Emissions Factors. U.S. Environmental Protection Agency. AP 42, Fifth Edition, Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources. Accessed multiple times during March and April 2013. <a href="http://cfpub.epa.gov/webfire/">http://cfpub.epa.gov/webfire/</a>

Haywood, personal communication. 2013. Personal communication from Jim Haywood, Meteorologist Specialist, MDEQ Air Quality Division; Author of the AERSCREEN model.

Kimbell, JS. 2006. Nasal Dosimetry of Inhaled Gases and Particles: Where Do Inhaled Agents Go in the Nose?, Toxicologic Pathology, 34:270–273